

CHAPTER 3

EXPERIMENTAL AND PROCEDURES

This chapter described all the experimental procedures employed in this work to synthesis, fabricate, characterize and measure the composite materials, with their physical and mechanical properties.

3.1 Synthesis of Carbon Nanotubes by Infusion CVD Method

The CNTs were synthesized in this experiment in accordance with the following procedure which is similar to the synthesis process of the CNTs reported by Singjai et al. [24] CNTs were synthesized by infusion CVD method using ethanol as the carbon source and nickel oxide as a catalyst. A schematic view of the infusion CVD apparatus is shown in Fig. 3.1. At the low temperature, the diffusion of carbon atom from Ni – C solid is easy [95]. From the previous research indicated that 700 °C is the best temperature for synthesis the CNTs because the several lengths of CNTs were obtained [96]. The experiment started with a valve-controlled gravity flow of infusing 0.33 ml/min ethanol into a tube furnace containing 2.5 g nickel oxide powder. The ethanol was then evaporated at its boiling temperature to a vapor form at a pressure in which the ethanol vapor-flowing tube furnace was occurred. Nickel oxide was reduced by the ethanol vapor at 450 °C for 30 min before the CNTs were synthesized at 700 °C for 9 h.

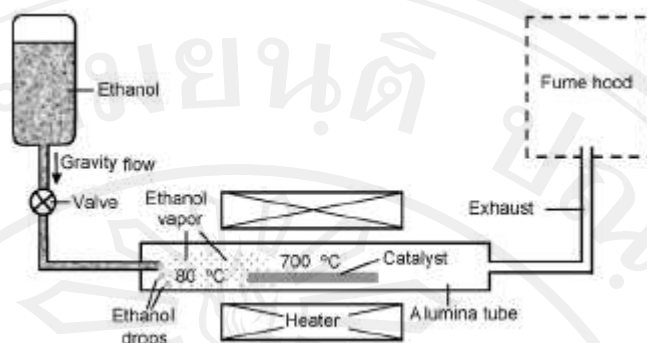


Figure 3.1 Schematic diagram of the infusion CVD apparatus [96]

The structure, morphology and quality of the as-prepared product were characterized by using scanning electron microscopy (SEM, JEOL JSM-6335F)

3.2 Synthesis of Silicon Carbide Nanowires (SiCNWs) by CVD Method

3.2.1 Without vacuum pump - assisted system

SiCNWs were synthesized in a horizontal alumina tube furnace. 0.375 g of purity Si powder (99%, Aldrich) and carbon powder (ultrahigh pure graphite 99.9%) was mixed with 0.20 g of NiO and first put into an alumina boat. The mixture was placed in the center of the tube furnace and activated carbon boat was put in 10 cm spacing. The tube was heated to 1,200 -1,400°C by rating of 10°C/min and kept for 1 h under argon flowing 2 L/min. SiC nanowires were formed. Finally, the furnace was cooled down to temperature by rating of 10°C/min. To purification SiC nanowires, the products were further heat treated at 700°C for 4 h in air to remove residual carbon. The obtained SiC nanostructures were characterized by a field-emission scanning electron microscopy, transmission electron microscopy. The crystallographic data was collected by X-ray diffraction.

3.2.2 With vacuum pump - assisted system

The SiC nanowires were synthesized in a horizontal alumina tube furnace. 0.03 mol of purity Si powder (99%, Aldrich) and 0.06 mol of carbon powder (ultra high pure graphite 99.9%) were mixed with 0.001 mol of Fe_2O_3 or Ni_2O_3 . The raw materials were mixed and pulverized in a mortar for 20 min. The mixed powders were filled into an alumina boat and placed in the center of the tube furnace. Then carbon boat was put in 5 cm spacing. The tube was pumped out initially by vacuum pump and high purity argon was released into the furnace for three times to estimate the residual air. After that, the furnace was heated with different reaction temperature of 1300°C , 1350°C and 1400°C by rating of $10^\circ\text{C}/\text{min}$ and kept for 1 h. SiC nanowires were formed. Finally, the furnace was cooled down to 300°C by rating of $10^\circ\text{C}/\text{min}$ and then cooled down to room temperature naturally. To purification the SiC nanowires, the products were further heat-treated at 700°C for 4 h in air to remove residual carbon.

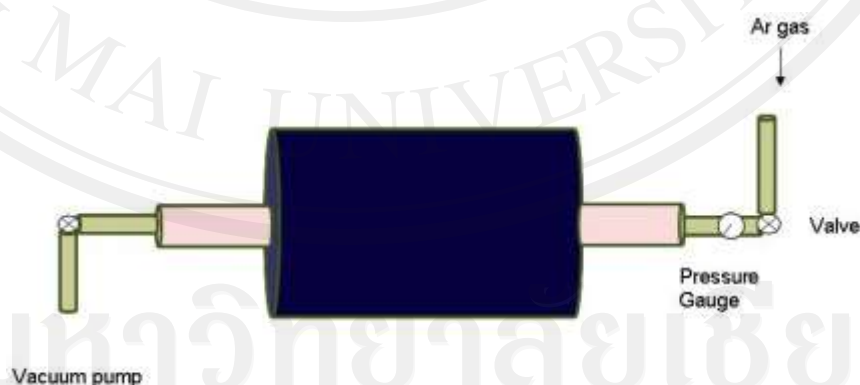


Figure 3.2 Schematic diagram of the synthesis SiCNWs by CVD method

The obtained SiC nanostructures were characterized by a field-emission scanning electron microscopy (SEM, JEOL JSM-6335F), transmission electron microscopy (TEM, JEOL JEM-2010). The crystallographic data was collected by X-ray diffraction and FTIR spectrum shows the absorption bands.

3.3 Fabrication of carbon nanotubes/silicon carbide nanowires/epoxy resin nanocomposites

The CNTs and SiCNWs were chemically treated by mixed acid 1 vol% of hydrofluoric acid and nitric acid at 200 °C for 2 h and left at room temperature until 24 h. Then the products were washed with distilled water until pH 7 and ethanol.

After filtration and a drying step at 100 °C for 4 h, the final products were obtained and used as reinforcements into epoxy resin.

Before the CNTs were mixed in the epoxy resin, these nano-products were ground for 10 min. In order to decrease agglomeration of SiCNWs powders, these products were ground through sieve 120 meshes. A matrix was created by mixing epoxy resin (#7275, Thai Epoxy Resin Ltd.,) with its hardener in the ratio 100:27 by volume. The density of the matrix is 1.176 g/cm³. To fabricate the composite samples, CNTs and SiCNWs were added into epoxy resin with the different ratios varying from 0.05 to 0.2 % by volume. The mixtures of epoxy resin and MWNTs were then dispersed for 3 h in an ultrasonic bath. Each mixture was filled with the hardener, sonicated for 5 min and poured down into the rubber mold as shown in fig. 3.3 and fig. 3.4. It is noted that mylar films were put at the upper and the lower of the samples in order to obtain a smooth surface. The composite samples were left to cure at the room temperature for 1 day and then removed from the mold.

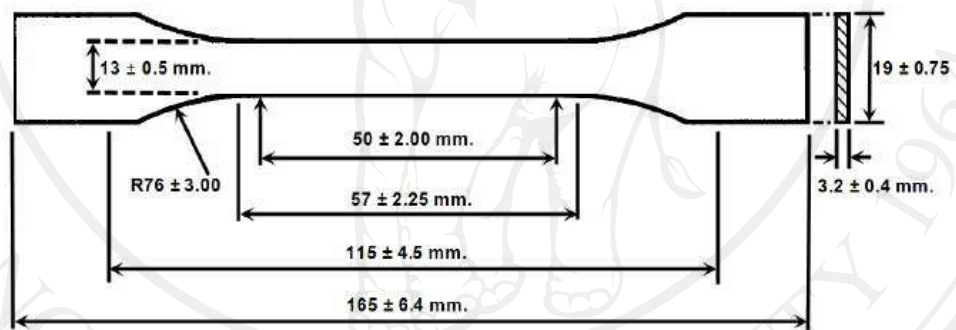


Figure 3.3 The rubber mold and sample geometry for tensile test [104]

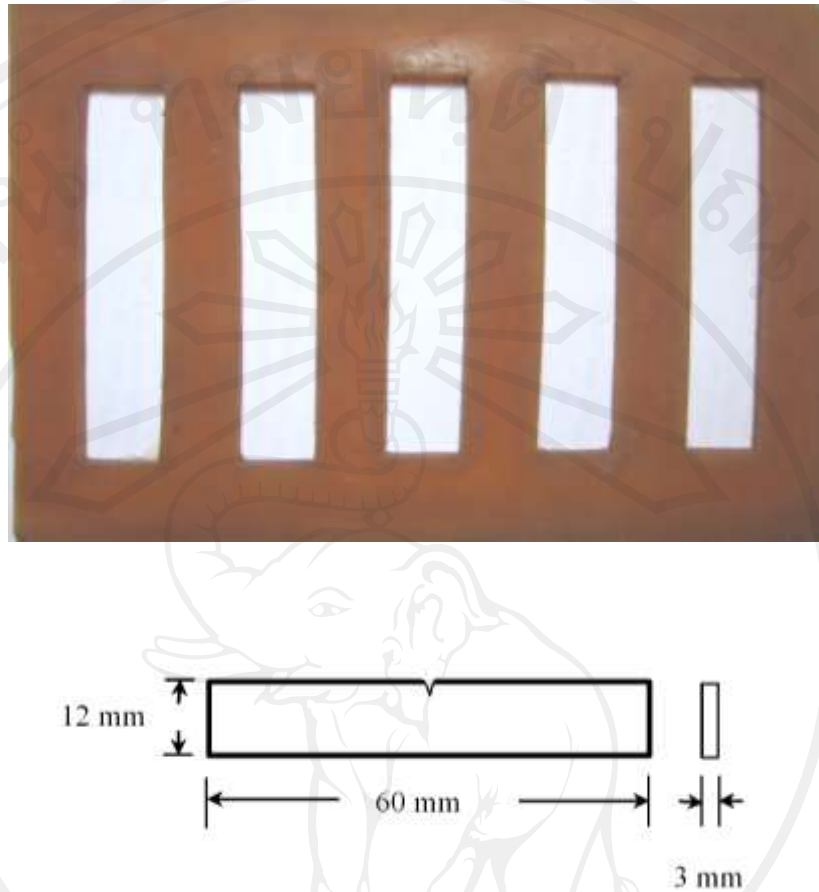


Figure 3.4 The rubber mold and sample geometry for impact test

Density of all composite samples was examined using Archimedes' method. Tensile and compressive strength of the samples were measured by the universal testing machine (Instron Instruments) with a cross-head rate at 1 mm/min. The compressive strength also was measured by the universal testing machine with rate 2 mm/min. Besides, impact strength of the samples were tested by Charpy method with Moreover, the microstructures of the composite samples were investigated by scanning electron microscopy (SEM).

3.4 Characterization and Measurement Methods

The follow section is intended to address the main characterization techniques used to investigate the phase formation, morphology, microstructure of the silicon carbide nanowires which used as the reinforcement phase in this work.

3.4.1 X-ray Diffraction Analysis

In this work, x-ray monochromater (XRD) was used to determine the phase and interplanar spacing (hkl) of the synthesized SiCNWs. A JEOL JDX- 8030 monochromater was conducted using $\text{CuK}\alpha$ radiation through a Ni filter (fig. 3.5).

The generator was operated at 40 kV and 20 mA. The XRD line profiles were obtained over a 2θ range of 20° - 90° , with a step of 5 degree and 1 sec counting time.

The results of XRD were compares with the JCPDS file in the database to determine the phase formation.



Figure 3.5 X-ray Monochromater

3.4.2 Scanning Electron Microscopy (SEM)

In this study, A JEOL JSM-6335F as shown in fig. 3.6 was used to determine the morphology of the CNTs and SiCNWs. The products were pasted on the brass sample holder and coated with gold via r-f sputtering techniques. During image acquisition, both backscattered and secondary electron modes were used with an accelerating voltage of 15 kV. Chemical composition of the selected area was quantified by using an energy dispersive (EDS)



Figure 3.6 Scanning electron microscopy (JEOL JSM-6335F)

3.4.3 Transmission Electron Microscopy (TEM)

A Transmission electron microscopy (TEM) was employed to investigate the morphology of the synthesized carbon nanotubes. Samples for TEM were prepared by grinding and dissolving the carbon nanotubes in ethanol, shaking by ultrasonic both, dropped the mixture on the copper grids, left it dry in the air. The samples were investigated by TEM (JEOL JEM-2010) operated at a 200 accelerating voltage (fig. 3.7).



Figure 3.7 Transmission electron microscopy

3.4.4 Energy Dispersive Spectroscopy (EDS)

Some SEM and TEM instruments have the very valuable additional feature of providing an elemental analysis of the samples composition. When a sample in the microscope is bombarded with high energy electrons, many things can happen, including the generation of X-rays. The X-rays are characteristic emission spectra of the elements present. By scanning either the wavelength (wavelength dispersive, WD) or the energy (energy dispersive, ED) of the emitted X-rays, it is possible to identify the elements presented in the samples. With suitable calibration, quantitative elemental analysis may be made.

3.5 Property Measurement of the Nanocomposites

The follow section is intended to address the main characterization techniques used to investigate physical and mechanical properties of the materials in this work.

3.5.1 Density Measurement

The density of all the composite samples was measured using the Archimedes' method. The samples were first weighed in the air (W_d). Then, they were immersed in the water for 1 hour at the room temperature. After that, the samples were weighed again in pure water to determine the wet weights (W_w) by suspending on a thin copper wire. All weights are in grams. The density was the calculated from the following equation [101]:

$$\sigma = \left(\frac{W_d}{W_d - W_w} \right) \sigma_w \quad (3.1)$$

where ρ_w is the density of the water (in g/cm^3), which is slightly temperature dependent,

$$\sigma_w = 1.0017 - 0.0002315T \quad (3.2)$$

when T is the temperature of the pure water (in degree Celsius) [102].



Figure 3.8 Density measurement

3.5.2 Tensile Strength Measurement

The test process involves placing the test specimen in the testing machine and applying tension to it until it fractures. During the application of tension, the elongation of the gage section is recorded against the applied force. The data is manipulated so that it is not specific to the geometry of the test sample. The elongation measurement is used to calculate the strain, ϵ , using the following equation:

$$\epsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0} \quad (3.3)$$

where ΔL is the change in gage length, L_0 is the initial gage length, and L is the final length. The force measurement is used to calculate the *stress*, σ , using the following equation:

$$\sigma = \frac{F_n}{A} \quad (3.4)$$

where F is the force and A is the cross-section of the gage section.

To investigate the mechanical properties, tensile strength by using the universal testing machine with a cross-head rate at 1 mm/min.



Figure 3.9 The universal testing machine

3.5.3 Compressive Strength Measurement

Compressive strength was measured by using the universal testing machine with compression rate at 2 mm/min



Figure 3.10 The universal testing machine for compression test

3.5.4 Impact Strength Measurement

Impact strength was measured by impact tester with Charpy impact test which determines the amount of energy absorbed by a material during fracture. At the point of impact, the striker has a known amount of kinetic energy. The impact energy is calculated based on the height to which the striker would have risen, if no test specimen was in place, and this compared to the height to which the striker actually rises. Tough materials absorb a lot of energy, whilst brittle materials tend to absorb very little energy prior to fracture. The absorbed energy is calculated using the following equation

$$AE \text{ (Absorbed Energy)} = E_p - E_p' \quad (3.5)$$

$$E_p' = \omega r(\cos\beta - \cos\alpha) = mgr(\cos\beta - \cos\alpha) \quad (3.6)$$

Where $E_p = 27.88 \text{ J}$

α = the angle of pendulum before impact (160.86°)

β = the angle of pendulum after impact

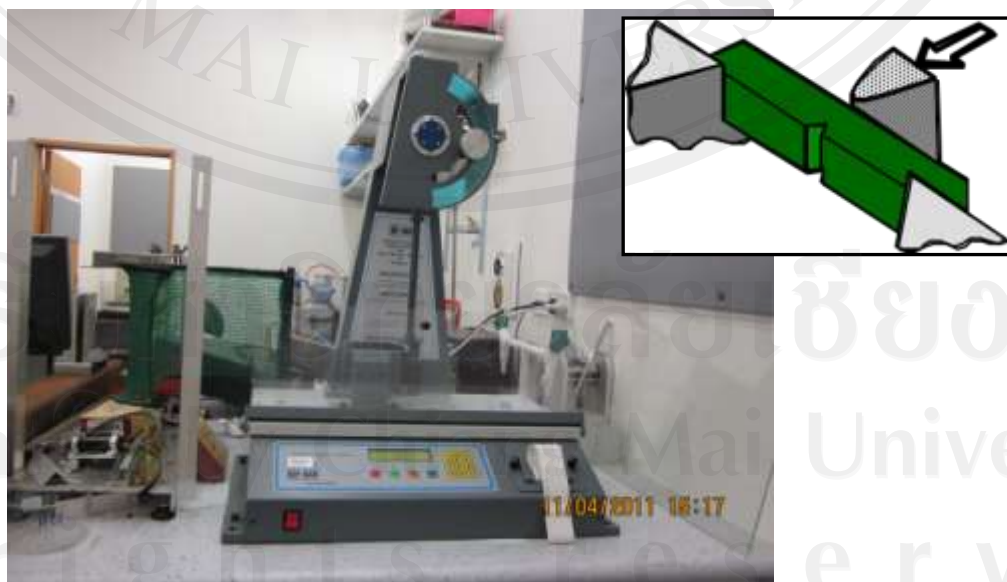


Figure 3.11 The apparatus of impact strength test

3.5.5 Wear Measurement

The wear resistance was measured by the Pin-on-Disk Tribometer (ISC-200-Tribometer) as shown in fig. 3.12. The samples, 12x12 mm, were pasted on the plastic sample holder. The condition used for this measure were a WC-Co ball which wear track radius 3 mm, load 500 g , turning 1500 turns and the sphere radius 3.175 mm. The wear tests were carried out at room temperature without the lubrication. The width track radius of all composite samples was measured and then the wear rate can be calculated from the following equations:

$$\text{wear rate} = \frac{\text{volume loss (mm}^3\text{)}}{\text{sliding distance (mm)}} \quad (3.7)$$

$$\text{when } \text{volume loss (mm}^3\text{)} = \frac{\pi(\text{wear track radius,mm})(\text{track width,mm})^2}{6(\text{sphere radius,mm})} \quad (3.8)$$

$$\text{sliding distance (mm)} = 2\pi rN \quad (3.9)$$

where N and r refer to the turning of the sample and the wear track radius.



Figure 3.12 Pin-on-Disk Tribometer